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WO 00/75415 A1

(54) Title: AN ARTICLE OF CLOTHING HAVING ANTIBACTERIAL, ANTIFUNGAL, AND ANTIYEAST PROPERTIES

(57) Abstract: The invention provides an article of clothing having antibacterial, antifungal, and antiyeast properties, comprising at least a panel of a metallized textile fabric, the textile fabric including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof, and having a plating including an antibacterial, antifungal and antiyeast effective amount of at least one oxidant cationic species of copper.

AN ARTICLE OF CLOTHING HAVING ANTIBACTERIAL, ANTIFUNGAL, AND ANTIYEAST PROPERTIES

Technical Field

The present invention relates to an article of clothing. More particularly, the present invention relates to an article of clothing, having antibacterial, antifungal and antiyeast properties.

In both WO 09/06508 and in WO 98/06509, the teachings of which are incorporated herein by references, the state of the prior art is described as follows:

Background Art

Beds commonly are infested by tiny mites. These mites eat bacteria and fungi that grow on epidermal scales shed by people who sleep in the beds. Fragments of dead mites and mite excreta, are allergens, to which asthmatics and people with dust allergens are sensitive. It has been found that some metals and metal oxides, notably Cu, CuO, Ag and Ag_2O, repel mites.

The conventional method for making textiles inhospitable to mites is to treat the textiles with an organic acaricide such as benzyl benzoate. For example, Bischoff et al., in U.S. Patent No. 4,666,940, teach an acaricide that includes benzyl benzoate and a solid powder carrier whose particles are of a size suitable for ingestion by the mites. These acaricides must be replaced every time the textile is laundered. Thus, Bischoff et al. recommend using their acaricide on textiles, such as carpets and upholstery, that are not laundered frequently. An inherently acaricidal bedsheet would keep a bed free of mites, even after multiple launderings, without the need to reapply acaricide to the bedsheet.

The methods known in the prior art for bonding a metal or a metal oxide to a textile generally require that the metal or its oxide be bonded indirectly to the textile. For example, the metal may be reduced to a powder and suspended in a binder. The binder-metal mixture then is applied to the textile, with the binder, and not the metal, bonding to the textile. Alternatively, the metal is reduced to a powder, an adhesive is applied to the textile, and the metal powder is spread on the adhesive. Examples of both such methods may be found in U.S. Patent No. 1,210,375, assigned to Decker. These methods are less than satisfactory for the above applications, for at least two reasons. First, the carrier or adhesive may entirely encapsulate the metal or metal oxide powder particles, inhibiting their contact with

mites, fungi and bacteria, and making the textile useless as an acaricide, fungicide, or bactericide. Second, multiple launderings tends to weaken the binder or adhesive and loosen or remove the particles.

Two notable exceptions to the general rule that metals and metal oxides have not heretofore been bonded directly to textiles are nylon textiles and polyester textiles, which may be plated with metals using standard electrolyses plating processes for plating plastics. The specific electrolyses plating methods known to the art are restricted in their applicability to only certain plastics, however. In particular, they are not suited to natural fibers, nor to most synthetic fibers.

With this state of the art in mind, both of said publications taught various aspects of a textile with a full or partial metal or metal oxide plating directly and securely bonded to the fibers thereof.

More specifically, in WO 98/06509 there is provided a process comprising the steps of: (a) providing a metallized textile, the metallized textile comprising: (i) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof, and (ii) a plating including materials selected from the group consisting of metals and metal oxides, the metallized textile characterized in that the plating is bonded directly to the fibers; and (b) incorporating the metallized textile in an article of manufacture.

In the context of said invention the term "textile" includes fibers, whether natural (for example, cotton, silk, wool, and linen) or synthetic yarns spun from those fibers, and woven, knit, and non-woven fabrics made of those yarns. The scope of said invention includes all natural fibers; and all synthetic fibers used in textile applications, including but not limited to synthetic cellulosic fibers (i.e., regenerated cellulose fibers such as rayon, and cellulose derivative fibers such as acetate fibers), regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, and vinyl fibers, but excluding nylon and polyester fibers, and blends thereof.

Said invention comprised application to the products of an adaptation of technology used in the electrolyses plating of plastics, particularly printed circuit boards made of plastic, with metals. See, for example, Encyclopedia of Polymer Science and Engineering (Jacqueline I. Kroschwitz, editor), Wiley and Sons, 1987,

vol. IX, pp 580-598. As applied to textiles, this process included two steps. The first step was the activation of the textile by precipitating catalytic noble metal nucleation sites on the textile. This was done by first soaking the textile in a solution of a low-oxidation-state reductant cation, and then soaking the textile in a solution of noble metal cations, preferably a solution of Pd++ cations, most preferably an acidic $PdCl_2$ solution. The low-oxidation-state cation reduces the noble metal cations to the noble metals themselves, while being oxidized to a higher oxidation state. Preferably, the reductant cation is one that is soluble in both the initial low oxidation state and the final high oxidation state, for example Sn++, which is oxidized to Sn++++, or Ti+++, which is oxidized to Ti++++.

The second step was the reduction, in close proximity to the activated textile, of a metal cation whose reduction was catalyzed by a noble metal. The reducing agents used to reduce the cations typically were molecular species, for example, formaldehyde in the case of Cu++. Because the reducing agents were oxidized, the metal cations are termed "oxidant cations" herein. The metallized textiles thus produced were characterized in that their metal plating was bonded directly to the textile fibers.

In preferred embodiments, said article of manufacture referred to therein.

In WO 98/06508 there is described and claimed a composition of matter comprising:

(a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and

(b) a plating including materials selected from the group consisting of metals and metal oxides;

the composition of matter characterized in that said plating is bonded directly to said fibers.

Said publication also claims a composition of matter comprising:

(a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and

(b) a plurality of nucleation sites, each of said nucleation sites including at least one noble metal;

the composition of matter characterized by catalyzing the reduction of at least one metallic cationic species to a reduced metal, thereby plating said fibers with said reduced metal.

In addition, said publication teaches and claims processes for producing said products.

A preferred process for preparing a metallized textile according to said publication comprises the steps of:

a) selecting a textile, in a form selected from the group consisting of yarn and fabric, said textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof;

b) soaking said textile in a solution containing at least one reductant cationic species having at least two positive oxidation states, said at least one cationic species being in a lower of said at least two positive oxidation states;

c) soaking said textile in a solution containing at least one noble metal cationic species, thereby producing an activated textile; and

d) reducing at least one oxidant cationic species in a medium in contact with said activated textile, thereby producing a metallized textile.

While the metallized fabrics produced according to said publications are effective acaricides, it has now been found that they are also effective in preventing and/or treating bacterial, fungal and yeast infections which afflict various parts of the human body and that therefore the incorporation of at least a panel of a metallized textile material in an article of clothing can have extremely beneficial effect.

Thus, for example, a large number of people suffer from discomfort in the crotch area with symptoms such as itching and skin rash due often to the buildup of undesirable fungus and bacteria. The fungus that causes the condition known as "Thrush" or yeast infection is *Candida Albicans*". While yeast infections are often internal they can also be external and manifest themselves with superficial lesions, itching, etc. *Tinea Pedis* can also appear in the crotch area of both women and men.

Therefore, an underwear that has a treated textile insert located in the crotch will attack dermatital fungi and relieve the wearer of uncomfortable fungal symptoms is sought and has now been found to be provided by the present invention.

Similarly, the fungus which causes Athletes foot is *Tinea Pedis*. The bacteria that cause foot odor are *brevibacterium, acinetobacter and micrococcus.*

It has been found that an article of hosiery, including at least a panel of metallized textile according to the present invention, is effective for treating and preventing Athletes foot and foot odor.

Similarly, articles of footwear such as cloth slippers and/or slippers having textile components, including at least a panel of metallized textile according to the present invention, are effective for treating and preventing Athletes foot and foot odor.

Furthermore, articles of headwear such as turbans and scarves, including at least a panel of metallized textile according to the present invention, are effective for treating and preventing odor and various skin diseases of the head.

Disclosure of the Invention

With this state of the art in mind, and after further research and development there is now provided according to the present invention an article of clothing having antibacterial, antifungal, and antiyeast properties, comprising at least a panel of a metallized textile fabric, said textile fabric including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof, and having a plating including an antibacterial, antifungal and antiyeast effective amount of at least one oxidant cationic species of copper, wherein the plating is directly bonded to the fibers.

The fabric can be made of almost any fiber, however, a certain percentage of the fibers in the yarn from which the fabric is made, is treated so that the fibers are coated with an ionic form of copper, e.g., CuO or Cu_2O. The copper is deposited through an oxidation reduction process on the fibers. The treated fibers are then mixed with regular untreated fibers and spun into yarns for introduction into a textile fabric fabric.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention

as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

EXAMPLE 1

Step A: A metallized fabric was prepared as described in Example 1 of WO98/06508.

A dilute acidic solution of $SnCl_2$ was prepared by dissolving $SnCl_2$ and concentrated HCl in water.

A dilute acidic solution of $PdCl_2$ was prepared by dissolving $PdCl_2$ 10 and concentrated HCl and water.

A cotton fabric 250x250 cm was activated as follows:

Soak in a bath of the $SnCl_2$ solution

Soak in a bath of the $PdCl_2$ solution.

A dilute basic $CuSO_4$ solution was prepared by dissolving $CuSO_4$ and NaOH (in approximately equal weight proportions), a chelating agent, and polyethylene glycol in water.

The activated cotton fabric and formaldehyde were added to the $CuSO_4$ solution under a pure oxygen atmosphere. After between 2 minutes and 10 minutes, the cotton fabric was removed.

The palladium deposited on the cotton fabric in the activation step catalyzed the reduction of the Cu++ by the formaldehyde, providing a layer of copper tightly and intimately bonded to the fibers of the cotton fabric. The fabric, which initially was white in color, now as the color of copper metal, while retaining the flexibility and physical characteristics of the original fabric. The metallic copper color remained unchanged after several launderings.

The configuration of the bath is such that in the Copper Sulfate step the fabric is set up vertically and not in the tradition horizontal pile to allow a clean reduction on to the fabric surface of the desired copper. The vertical positioning of the fabric is done with the aid of or plurality of poles set up on a frame in an array

similar to two spaced-apart rung ladders with the poles acting as said rungs. The fabric is interwoven in a repeating switchback array on the poles of the frame in such a way that at no place does the fabric touch other parts of the fabric. This configuration also allows the escape of gases as the chemicals react with one another thereby yielding a clean copper reduction on the fabric.

EXAMPLE 2

The procedure of Example 1 was repeated using cotton yarn in place of cotton fabric. Yarn for weaving into a woven cloth was prepared from fibers which received 100% coating, which treated fibers were then combined in a ratio of 20 w/w% with 80% untreated fibers to form a yarn containing 20% copper. These yarns were then introduced as the weft (fill) yarn with warp threads, which were untreated, to produce panels of fabric containing 10% Cu++. This fabric was then tested for anti-fungal and anti-microbial activity, the results of which are reported in the Examples hereinafter.

Example 3 Antifungal susceptilibility testing.

Susceptibility testing was performed as follows:

Agar formulation used for this test was chosen in accordance with NCCLS document M27-A: RPMI 1640 medium (Sigma, St. Louis, Mo.) supplemented with 1.5% agar and 2% glucose (RPG) and buffered to pH 7.0 with 0.165 M morpholinepropanesulfonic acid buffer (MOPS). For the test, 90-mm-diameter plates containing agar at a depth of 4.0 mm were used. For *Candida albicans, and Cryptococcus neoformans*, the inoculum was prepared from a 24 hr. culture and a 48 hr. culture, respectively; where for *Aspergillus fumigatus and Trichophyton mentagrophytes* a five-day old culture was used. Cell suspension was prepared in sterile 0.85% NaCl adjusted to a turbidity of a 0.5 Mc-Farland standard. The agar surface was inoculated by streaking a nontoxic swab dipped in a cell suspension across the entire surface of the agar in three directions. After excess moisture was absorbed into the agar and the surface was completely dry, panels of fabric prepared according to Example 2 and containing ionic copper-treated fibers in a concentration range of 3-10% were applied to each plate. The plates were incubated at 35°C and read after 24 hr, 48 hr, and 7 days. Antifungal activity of the fabric was considered as positive if a zone of inhibition was visible underneath and surrounding the fabric.

Example 4 Antibacterial susceptibility testing.

Susceptibility testing was performed as described above for the antifungal activity in Example 3 with the following modifications:

Mueller-Hinton agar (Difco, Detroit, MI) was the medium used. The pH was adjusted to 7.2-7.4. The bacteria used for this study were *Escherichia coli* and *staphylococcus aureus.*

Results:

The fabric containing ionic copper treated fibers subjected to the susceptibility of tests of Examples 3 and 4 in a concentration range of 3-10% exhibited characteristic inhibitory zone underneath and surrounding the fabric in each of the plates and in all of the concentrations tested, indicating its wide range of antifungal and antibacterial activity.

Example 5

Antifungal (Candida) Susceptibility report
Test Results

RESULTS OF FUNGAL TESTING DONE AT HADASSAH HOSPITAL MEDICAL SCHOOL ON SEPTEMBER 18, 1999.

The following is a review of the procedure, description of samples, and charts showing the results of fungal testing for the efficacy of Cu++ impregnated fabrics after a series of industrial washings. The results in this test are for the fungus *Candida Albicans.*

1. Procedure

All tests follow the AATCC Method for Testing Anti-Fungal Activity in Textile fabrics.

II. Description of samples

Cellulose fibers were treated and coated with Cu++, as described in Example 2. These fibers were then mixed with a normal length (38 mm) cotton fiber.

The woven fabric in the test was made from a yarn from a mixture of 20% treated fibers mixed with 80% normal fibers (measured by weight) and spun into 24/1's prepared for weaving. The yarn was twisted to about 100 twists per meter. The yarn was introduced into the fill only of a 50% cotton/50% polyester warp yielding a 75% cotton/25% polyester fabric with a finished weight of about 4.5 oz. per square yard. The fabric was desiezed using a warm water soapy solution and treated with BF Goodrich's Acrylic Solution Printrite 595 after being diluted 9:1

(water:acrylic). The fabric was heat-set at over 125 degrees Centigrade through the use of hand iron.

The knit fabrics in the test were a mixture of 15% treated fibers mixed with 85% normal fibers (by weight) and spun into 22/1's prepared for knitting with a paraffin coating. The yarn was twisted to about 500 twists per meter. The yarn was introduced into two different types of socks. One sock was a flat knit with an exchange of one treated/one untreated yarn. The second sock was a standard terry cloth sport sock. All loops and base yarns were the treated yarns. The socks according to the present invention will be referred to hereinafter by the tradename CureTex.

As is standard procedure in the manufacture of socks, the socks were washed at 40°C and pressed.

One sock each of a Sanitized (navy color), Amicor (white color but Amicor treated yarns are yellow), ***CureTex*** elegant sock (dark grey sock with ***CureTex*** yarns which are light grey), ***CureTex*** sport sock (white sock with ***CureTex*** yarns which are light grey) along with a piece of untreated woven fabric were sewn together along the top of the sock so that when the socks and woven fabric were washed, all samples went though identical
conditions.

Each sample in the sewn together group was identified with a letter for identification. The fabrics were washed at 60°C (140°F) using a mild detergent and were washed in full loads at a commercial laundry in Bet Shemesh. The garments were then dried for 45 minutes after each washing in a full commercial gas tumble dryer. After each washing a sample was cut from each article and placed in an envelope with the number of wash cycles on the envelope and the date.

III.Test Procedure

Pieces of about 1 square centimeter were cut from each sock and fabric after wash/dry cycle numbers: 1,2,3,4,5,10,15,20. Each fabric was marked and placed in the same petri dish as all others in the same wash/dry cycle. Separate petri dishes were prepared for an additional woven sample that was treated with the BF Goodrich Acrylic PrintRite 595 as described above as well as a dish for a 0.25% nylon yarn supplied by Bonazzi of Italy, a 1% nylon yarn supplied by Bonazzi of

Italy, and a Nike Sanitized treated sock (new) supplied to us by Gibor Socks of Israel.

Samples are identified as follows:

I. Sanitized (navy) – This is a sample from a sock using the Sanitized finish. This sock was supplied to us by a leading manufacturer of this product. This is a topical chemical treatment placed after manufacture of the sock.

II. Woven 20% untreated ***CureTex*** – This is a woven sample made from a 20% treated/80% untreated fiber inserted in the fill made for us by Springfield of the USA. This sample has gone through washing cycles and was produced with no finish on it at all.

III. Amicor (white/yellow fiber) – This is a sample from a sock using an organic compound introduced in slurry state in an acrylic based fiber. The sock was supplied to us by a leading manufacturer of this product.

IV. ***CureTex*** 15% (dark grey/light grey fiber) – This is a sample from a sock using a 15% treated/ 85% untreated fiber. This sock was made in the same density as the sock in sample A (Sanitized) and was produced by the same manufacturer as sample A.

V. ***CureTex*** 15% (white/light grey fiber) – This is a sample from a sock using a 15% treated/ 85% untreated fiber. This sock was made in the same density as the sock in sample C (Amicor).

VI. Control (plain cotton)

These letters form the columns of the following chart.

Washing cycles are identified as:

1. 1 wash cycle
2. 2 wash cycles
3. 3 wash cycles
4. 4 wash cycles
5. 5 wash cycles
6. 10 wash cycles
7. 15 wash cycles
8. 20 wash cycles

These numbers form the lines of the following chart.

All fabrics that went through the same procedures were tested together in the same petri dish to facilitate an objective comparison of results.

Test Result Chart

Petri Dishes with Multiple Samples

	A Sanitized Navy	B *CureTex* Woven	C Amicor White Terry	D *CureTex* Dark Grey	E *CureTex* White Terry
1. 1 cycle	++	++	+	++	+++
2. 2 cycles	+	++	+	+++	+++
3. 3 cycles	+	+++	+	+++	+++
4. 4 cycles	+-	+++	-	+++	+++
5. 5 cycles	-	+++	+	+++	+++
6. 10 cycles	+	+++	+	+++	+++
7. 15 cycles	+	+++	-	+++	+++
8. 20 cycles	+	+++	-	+++	+++

All controls registered no anti-fungal activity (-)

Code to symbols:

(-) indicates no anti-fungal activity

(+) indicates very poor anti-fungal activity or hardly noticeable activity

(++) indicates partial anti-fungal activity

(+++) indicates full anti-fungal activity with a clear zone of inhibition

A second series of tests was conducted to see indicate efficacy of individual samples as follows:

Test Result Chart	
Petri Dishes with Single Samples	
The 20% Acrylic coated fabric with no washing:	+++
The Nike Sanitized sock fabric with no washing:	+
The 0.25% Nylon fiber:	+
The 1% Nylon fiber:	No result

Notes concerning above:

The 20% Acrylic coated fabric with no washing was a test to see if there was a reduction of biological activity due to the additional chemistry. The 20% blend piece was used because a clear copper identification could be made by a spectrometer attached to an electron microscope.

The Nike Sanitized sock was given to us for testing by the Nike licensee in Israel. This finish is a Sanitized sock which did not show any unexpected or exceptional results.

The 0.25% and the 1% Nylon are indications of blend levels of powdered Cu++ were added to nylon in resin state and then extruded into fiber. The fiber was supplied by Bonazzi of Italy. It should also be noted that the color of the 0.25% changed to a white shade indicating a leaching of the chemistry with the resulting efficacy. The color of the 1% remained the original pink shade and appeared not to be touching the agar which would indicate a fault in the test. This test should be redone.

All petri dishes were photographed for confirmation.

Amendment to test – October 12, 1999

Additional tests were conducted during the week of October 5th. The two fabrics tested were a disperse dyed Yellow (identified as "Yellow") 20% blend received from Springs and not washed. The second sample was a 20% blend fabric that was washed 35 times.

Yellow	++
20% blend 35 washings	++

Conclusions:

It is apparent that the ***CureTex*** samples demonstrate exceptional resistance to *Candida Albicans* even after 35 washings. The above test data demonstrates

limited efficacy against *Candida Albicans* by the Sanitized or Amicor products. The large zone of inhibition created by the ***CureTex*** samples indicate a leaching of the chemistry from the fabric (or yarn). This leaching would be an indication of the products ability to be delivered to skin surfaces and therefore able to remove fungus from the skin surface of the wearer.

Example 6

Antifungal (Trichophyton Mentagrophytes) Susceptibility report

Test Results

RESULTS OF FUNGAL TESTING DONE AT HADASSAH HOSPITAL MEDICAL SCHOOL DURING THE WEEK OF OCTOBER 5TH AND EXAMINED FOR RESULTS ON OCTOBER 12TH, 1999.

The following is a review of the procedure, description of samples, and charts showing the results of fungal testing for the efficacy of Cu++ impregnated fabrics after a series of industrial washings. The results in this test are for the fungus *Trichophyton mentagrophytes.*

2. Procedure

All tests follow the AATCC Method 30-1993 for Testing Anti-Fungal Activity in Textile fabrics.

II. Description of samples

Cellulose fibers were treated and coated with Cu++, as described in Example 2. These fibers were then mixed with a normal length (38 mm) cotton fiber.

The woven fabric in the test was made from a yarn from a mixture of 20% treated fibers mixed with 80% normal fibers (measured by weight) and spun into 24/1's prepared for weaving. The yarn was twisted to about 100 twists per meter. The yarn was introduced into the fill only of a 50% cotton/50% polyester warp yielding a 75% cotton/25% polyester fabric with a finished weight of about 4.5 oz. per square yard. The fabric was desiezed using a warm water soapy solution and treated with BF Goodrich's Acrylic Solution Printrite 595 after being diluted 9:1 (water:acrylic). The fabric was heat-set at over 125 degrees Centigrade through the use of hand iron.

The knit fabrics in the test were a mixture of 15% treated fibers mixed with 85% normal fibers (by weight) and spun into 22/1's prepared for knitting with a paraffin coating. The yarn was twisted to about 500 twists per meter. The yarn was

introduced into two different types of socks. One sock was a flat knit with an exchange of one treated/one untreated yarn. The second sock was a standard terry cloth sport sock. All loops and base yarns were the treated yarns.

As is standard procedure in the manufacture of socks, the socks were washed at 40°C and pressed.

One sock each of a Sanitized (navy color), Amicor (white color but Amicor treated yarns are yellow), ***CureTex*** elegant sock (dark grey sock with ***CureTex*** yarns which are light grey), ***CureTex*** sport sock (white sock with ***CureTex*** yarns which are light grey) along with a piece of untreated woven fabric were sewn together along the top of the sock so that when the socks and woven fabric were washed, all samples went though identical
conditions.

Each sample in the sewn together group was identified with a letter for identification. The fabrics were washed at 60°C (140°F) using a mild detergent and were washed in full loads at a commercial laundry in Bet Shemesh. The garments were then dried for 45 minutes after each washing in a full commercial gas tumble dryer. After each washing a sample was cut from each article and placed in an envelope with the number of wash cycles on the envelope and the date.

III.Test Procedure

Pieces of about 1 square centimeter were cut from each sock and fabric after wash/dry cycle numbers: 1,2,3,4,5,10,15,20. Each fabric was marked and placed in the same petri dish as all others in the same wash/dry cycle. Separate petri dishes were prepared for an additional woven sample that was treated with the BF Goodrich Acrylic PrintRite 595 as described above as well as a dish for a 0.25% nylon yarn supplied by Bonazzi of Italy, a 1% nylon yarn supplied by Bonazzi of Italy, and a Nike Sanitized treated sock (new) supplied to us by Gibor Socks of Israel.

Samples are identified as follows:

VII. Sanitized (navy) – This is a sample from a sock using the Sanitized finish. This sock was supplied to us by a leading manufacturer of this product. This is a topical chemical treatment placed after manufacture of the sock.

VIII. Woven 20% untreated ***CureTex*** – This is a woven sample made from a 20% treated/80% untreated fiber inserted in the fill made for us by Springfield of the

USA. This sample has gone through washing cycles and was produced with no finish on it at all.

IX. Amicor (white/yellow fiber) – This is a sample from a sock using an organic compound introduced in slurry state in an acrylic based fiber. The sock was supplied to us by a leading manufacturer of this product.

X. ***CureTex*** 15% (dark grey/light grey fiber) – This is a sample from a sock using a 15% treated/ 85% untreated fiber. This sock was made in the same density as the sock in sample A (Sanitized) and was produced by the same manufacturer as sample A.

XI. ***CureTex*** 15% (white/light grey fiber) – This is a sample from a sock using a 15% treated/ 85% untreated fiber. This sock was made in the same density as the sock in sample C (Amicor).

XII. Control (plain cotton)

These letters form the columns of the following chart.

Washing cycles are identified as:

9. 1 wash cycle
10. 2 wash cycles
11. 3 wash cycles
12. 4 wash cycles
13. 5 wash cycles
14. 10 wash cycles
15. 15 wash cycles
16. 20 wash cycles

These numbers form the lines of the following chart.

All fabrics that went through the same procedures were tested together in the same petri dish to facilitate an objective comparison of results.

Test Result Chart

Petri Dishes with Multiple Samples

	A Sanitized **Navy**	B *CureTex* Woven	C Amicor White Terry	D *CureTex* Dark Grey	E *CureTex* White Terry
1. 1 cycle	++	+++	++	+++	+++
2. 2 cycles	++	++	++	++	++
3. 3 cycles	++	+++	++	++	++
4. 4 cycles	++	++	++	++	++
5. 5 cycles	+	++	+	++	++
6. 10 cycles	+	++	++	++	+
7. 15 cycles	+	+	+	+	+
8. 20 cycles	+	++	++	++	++

All controls registered no anti-fungal activity (-)

Code to symbols:

(-) indicates no anti-fungal activity

(+) indicates very poor anti-fungal activity or hardly noticeable activity

(++) indicates partial anti-fungal activity

(+++) indicates full anti-fungal activity with a clear zone of inhibition

A second series of tests was conducted to see indicate efficacy of individual samples as follows:

Test Result Chart	
Petri Dishes with Single Samples	
The Yellow dispersed dyed by Springs no washing:	+
The Nike Sanitized sock fabric with no washing:	++
The 0.25% Nylon fiber:	+
The 1% Nylon fiber:	+

Notes concerning above:

The Yellow dispersed dyed fabric by Springs was a test sample that was dyed and unwashed to test biological activity. This fabric was a 20% blend piece.

The Nike Sanitized sock was given to us for testing by the Nike licensee in Israel. This finish is a Sanitized sock which did not show any unexpected or exceptional results. The sock was unwashed.

The 0.25% and the 1% Nylon are indications of blend levels of powdered Cu++ added to nylon in resin state and then extruded into fiber. The fiber was supplied by Bonazzi of Italy. It should also be noted that the color of the 0.25% changed to a white shade indicating a leaching of the chemistry with the resulting efficacy. The color of the 1% also turned white. Poor biological activity was observed on both samples.

All petri dishes were photographed for confirmation.

Conclusions:

CureTex is effective against *Trichophyton mentagrophytes.* It appears that the competitive products are less effective than ***CureTex*** in the inhibition of *Trichophyton mentagrophytes* but do show an improvement in general efficacy when compared to tests done on *Candida Albicans.*

Example 7

Bactericide and Fungicide Testing 3% and 5% Mix Blends

100% Cotton yarns spun in 30/1 English Count

Knit in standard jersey and sock forms

Antifungal Susceptibility Testing

Susceptibility testing was performed as follows:

Agar formulation used for this test was chosen in accordance with NCCLS document M27-A: RPMI (RPG) and a buffered to pH 7.0 with 0.165 M morpholinepropanesulfonic acid buffer (MOPS).

For the test, 90-mm-diameter plates containing agar at a depth of 4.0 mm were used. For *Candida albicans, Cryptococcus neoformans, micrococcus, Tinea pedis,* and *Tinea curpus,* the inoculum was prepared from a 24 hours culture and a 48hour culture respecitvely; whereas for *Aspergillus fumigatus* and *Trichophyton mentagrophytes* a five-day old culture was used. Cell suspension was prepared in stile 0.85% NaCl adjusted to a turbidity of a 0.5 McFarland standard. The agar surface was inoculated by streaking a nontoxic swab dipped in a cell suspension across the entire surface of the agar in three directions. After excess moisture was absorbed into the agar and the surface was completely dry, Chemtex/MTC treated fibers in a concentration range from 3%-10% were applied to each plate. The plates were incubated at 35 °C and read after 24 hours, 48 hours, and 7 days. Antifungal activity of the treated fibers was considered positive if a zone of inhibition was visible underneath and surrounding the fibers.

Antibacterial Susceptibility Testing

Susceptibility testing was performed as described above for the antifungal activity with the following modifications: "Mueller-Hinton agar (Difco, Detroit, MI) was the medium used. The pH was adjusted to 7.2-7.4.The bacteria used for this study were *Escherichia coli, Staphylococcus aureus, brevubacterium, acinetobacter* and *micrococcus.*

Results

The treated fibers in a concentration range of 3-10% exhibited characteristic inhibitory zone underneath and surrounding the fibers, indicating correct antifungal and antibacterial activity. The controls (untreated fibers) indicated no antifungal or antibacterial activity.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes

which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

WHAT IS CLAIMED IS:

1. An article of clothing having antibacterial, antifungal, and antiyeast properties, comprising at least a panel of a metallized textile fabric, said textile fabric including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof, and having a plating including an antibacterial, antifungal and antiyeast effective amount of at least one oxidant cationic species of copper.

2. An article of clothing according to claim 1, wherein said textile fabric is a woven fabric.

3. An article of clothing according to claim 1, wherein said textile fabric is a non-woven fabric.

4. An article of clothing according to claim 1, wherein said article is an article of hosiery.

5. An article of clothing according to claim 1, wherein said article is an undergarment.

6. An article of clothing according to claim 1, wherein said article is an undergarment and said panel is positioned in the crotch area thereof.

7. An article of clothing according to claim 1, wherein said article is a head covering.

8. An article of clothing according to claim 1, wherein said article is an article of footwear.

9. An article of clothing according to claim 8, wherein said article of footwear is a slipper.

10. An article of clothing according to claim 1, wherein said article is effective against *Tinea Pedis*.

11. An article of clothing according to claim 1, wherein said article is effective against bacteria causing foot odor, selected from the group consisting of *brevubacterium, acinetobacter, micrococcus* and combinations thereof.

12. An article of clothing according to claim 1, wherein said article is effective against *Candida Albicans*.

13. An article of clothing according to claim 1, wherein said article is effective against *Thrush*.

INTERNATIONAL SEARCH REPORT

Int tional Application No
PCT/IL 00/00290

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06M11/83

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 06509 A (MTC LTD ;GABBAY JEFFREY (IL)) 19 February 1998 (1998-02-19) cited in the application the whole document	1-13
X	US 5 458 906 A (LIANG PAUL M S) 17 October 1995 (1995-10-17) column 1, line 64 -column 2, line 23 examples claims 1-5	1-13
A	US 5 856 248 A (WEINBERG AMOTZ) 5 January 1999 (1999-01-05) column 2, line 49 -column 3, line 4 examples claims 1-5	1-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 September 2000	14/09/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IL 00/00290

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9806509 A	19-02-1998	US 5981066 A	09-11-1999
		AU 4052797 A	06-03-1998
		US 5939340 A	17-08-1999
US 5458906 A	17-10-1995	NONE	
US 5856248 A	05-01-1999	NONE	